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Grain growth of ZnO in binary ZnO-V_2O_5 ceramics

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Grain growth of ZnO during liquid-phase sintering of binary ZnO-V_2O_5 ceramics has been studied for V_2O_5 contents from 0.5 to 4 mol% and sintering from 900°C to 1200°C. The results are discussed and compared with previous studies in terms of the phenomenological kinetic grain growth expression:

$$G^n - G_o^n = K_o t \exp(-Q/RT).$$

Addition of V_2O_5 is found to decrease the ZnO grain growth exponent, *n*, as well as the apparent activation energy, *Q*. The activation analysis also reveals a change in the rate-controlling mechanism for ZnO grain growth. Following a low-V_2O_5-content ($\leq$2 mol%) of nearly constant *Q* values of about 88 kJ/mol, further V_2O_5 additions cause an increase of the *Q* value to about 115 kJ/mol. Consistent with accepted models of liquid-phase sintering, it is concluded that the rate-controlling mechanism of ZnO grain growth during liquid-phase sintering in the presence of V_2O_5 changes from one of a phase-boundary reaction at low V_2O_5 levels to one of diffusion through the liquid phase at more than 2 mol% V_2O_5 levels.

1. Introduction

Zinc oxide ceramic varistors derive their non-linear current-voltage behaviour from the addition of small amounts of other metal oxides, such as Bi_2O_3, Pr_6O_{11}, MnO_2 and Co_3O_4 [1–7]. Until recently, it was believed that effective varistor-forming ingredients were heavy elements with large ionic radii, such as bismuth [2, 3], praseodymium [4, 5], and barium [6, 7], but studies have now shown that the ZnO-V_2O_5 system also exhibits varistor behaviour [8–17]. This system is of interest because the ceramic can be sintered at a relatively low temperature of about 900°C. This is important for applications in which it can be a multi-layered chip component, because it can be co-fired with a silver inner-electrode (m.p. 961°C) without using the expensive palladium or platinum metals.

Electrical properties of these ZnO ceramic varistors are directly dependent on the microstructure as the ZnO grain size affects the varistor breakdown voltage per unit thickness [1–7]. There have been a number of studies addressing the sintering and grain growth of pure ZnO [18, 19] and the ZnO-Bi_2O_3 ceramic system [20–22], as it is important to fundamentally understand the microstructural development of ZnO ceramics. Although there have been studies investigating the grain growth phenomenon in ZnO with V_2O_5 additions [10], activation analyses of grain growth have not been attempted. Other than our preliminary report on a ZnO-1 mol% V_2O_5 ceramic [23], the role of V_2O_5-rich phase as it affects the grain growth kinetics of ZnO has not been quantitatively documented. In view that V_2O_5-doped ZnO varistors have the potential of replacing Bi_2O_3-doped ZnO varistors due to its low sintering temperature, a detailed analytical study of the ZnO grain growth in the ZnO-V_2O_5 ceramic system has to be done.

Hence, in this work, we will address the effects of V_2O_5 additions (0.5 to 4 mol%) in a quantitative manner by using an activation analysis of the kinetic parameters of ZnO grain growth, specifically the kinetic grain-growth exponent and the apparent activation energy for grain growth. These parameters are obtained from the phenomenological kinetic grain growth equation [21, 22]:

$$G^n - G_o^n = K_o t \exp(-Q/RT) \tag{1}$$

where G is the average grain size at time t, the n value is the kinetic grain growth exponent, K_o is the pre-exponential constant of the material, Q is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. In this study, the initial grain size, G_o, is significantly smaller than the grain size, G, at some later time. Thus, G_o can be neglected, and Equation 1 simplifies to

$$G^n = K_o t \exp(-Q/RT) \tag{2}$$

which will be used throughout this study.

2. Experimental procedures

High purity oxide powder starting materials were used for the preparation of the ZnO-V_2O_5 samples. Four

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compositions, 0.5, 1, 2 and 4 mol% V_2O_5 were investigated. The powder mixtures were ball-milled for 24 hrs using alumina balls in deionised water. The mixtures were filtered, dried and pressed into pellets of 13 mm diameter and 3 mm thickness. The pellets were then sintered at four temperatures (900, 1000, 1100 and 1200°C) for 4 hrs. Another series of specimens are sintered at 900°C for five different times (0.5, 1, 2, 4 and 8 hrs). Heating and cooling rates of 5°C/min were used. According to the ZnO-V_2O_5 phase diagram [24, 25], ZnO has a eutectic reaction with $Zn_3(VO_4)_2$ at ∼890°C. Thus, sintering temperatures $\geq$900°C were chosen in this study to ensure that the vanadium-rich liquid phase will enhance the densification of the samples. Densities were calculated from the weights and dimensions of the ceramic bodies.

Microstructures of the samples were observed using a scanning eletron microscope (JEOL JSM-5310) operated at 20 kV. The sintered specimens were cut diametrically using low speed diamond saw, and mounted with conductive resin. The samples were then ground with 600–1000 grit SiC paper, and finally polished to 1 μm surface finish using diamond paste. The surface were etched with 2% nital for about 1 min. Grain sizes were measured directly from the micrographs of the etched samples by the linear intercept technique described by Mendelson [26]. The average grain size, G, was obtained as

$$G = 1.56\,\bar{L} \tag{3}$$

where $\bar{L}$ is the average grain-boundary intercept length of a series of random lines on the micrographs.

3. Results

3.1. Density

Relative densities of the various ZnO-V_2O_5 samples sintered at different temperatures and times are shown in Fig. 1. Densities of the four systems remained rather constant over the range of sintering times studied (Fig. 1a). However, the relative density decreased with increasing sintering temperature (Fig. 1b), which is most probably due to volatility of V_2O_5 at high temperature. This was also observed by Tsai and Wu [9] in their ZnO-V_2O_5 binary systems.

3.2. Microstructural observations

Microstructural features of all the sintered ZnO-V_2O_5 samples are similar, except for the average ZnO grain size. They showed the following features: (1) large grains dispersed in a matrix composed of small grains and (2) the large grains having oblong shape. Such exaggerated ZnO grain growth was often found in V_2O_5-doped ZnO ceramics [8–17]. It was the high reactivity of the vanadium-rich liquid phase during sintering which caused such abnormal grain growth. However, the microstructure becomes more uniform as sintering temperature and time increases.

Microstructures of the series of ZnO-V_2O_5 ceramics sintered at 900°C for 8 hrs are illustrated in Fig. 2. The average ZnO grain size initially increases with increasing V_2O_5 content up to 2 mol%. A further increase of V_2O_5 content to >2 mol% causes a decrease in the grain size (Fig. 3). Tsai and Wu [9] also reported a similar trend for the effect of V_2O_5 on the grain growth of ZnO. They reported that ZnO grain growth is enhanced over that of pure ZnO with only a 0.25 mol% addition of V_2O_5, and observed a reduction of grain size at 2 mol% V_2O_5. However, they did not complete an activation analysis to identify the rate-controlling mechanism. It is reasonable to expect that this change in trend of the final grain size may correspond to a transition in the rate-controlling mechanism of the ZnO grain growth.

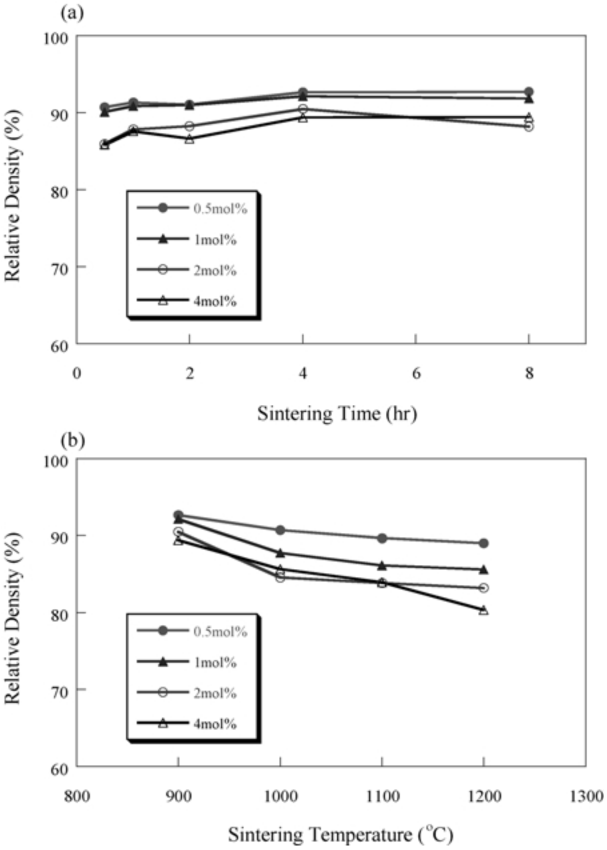

Figure 1 Effect of sintered density of ZnO-V_2O_5 samples with (a) sintering time (sintered at 900°C) and (b) sintering temperature (sintered for 4 hrs).

3.3. Activation analysis of kinetic grain-growth parameters

The phenomenological kinetic grain growth equation given by Equation 2 can be readily plotted in the form:

$$\log G = \frac{1}{n}\log t + \frac{1}{n}\left[\log K_{\text{o}} - 0.434\left(\frac{Q}{RT}\right)\right] \tag{4}$$

From the slope of the log G versus log t line, which is $1/n$, the grain growth kinetic exponent n is readily determined. Fig. 4 illustrates the isothermal grain growth results for the various ZnO-V_2O_5 samples sintered at 900°C in the form of Equation 4. The n value varies with V_2O_5 content, as summarised in Table I. Samples containing 0.5, 1 and 2 mol% V_2O_5 content have similar n values ranging between 1.5 to 1.8, while sample containing 4 mol% V_2O_5 has a higher n value of 2.69. Our previous work [23] on ZnO-1 mol% V_2O_5 showed a n

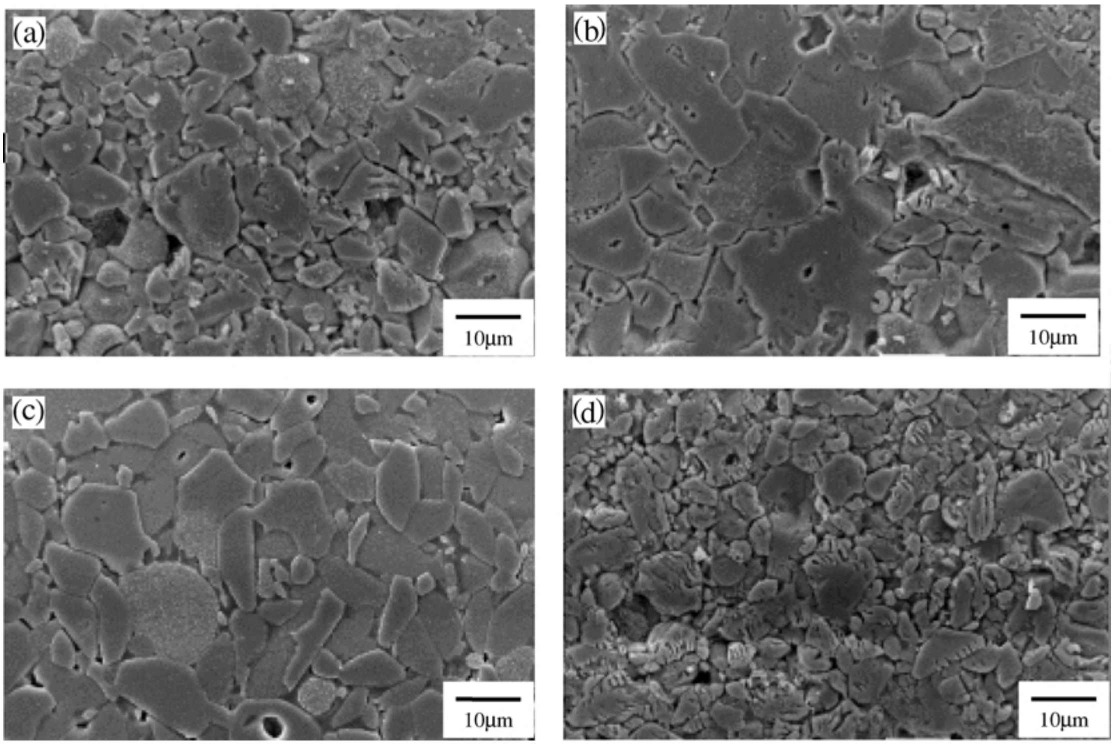

Figure 2 Microstructures in the ZnO-V_2O_5 systems sintered at 900°C for 8 hrs: (a) 0.5 mol% V_2O_5, (b) 1 mol% V_2O_5, (c) 2 mol% V_2O_5, and (d) 4 mol% V_2O_5.

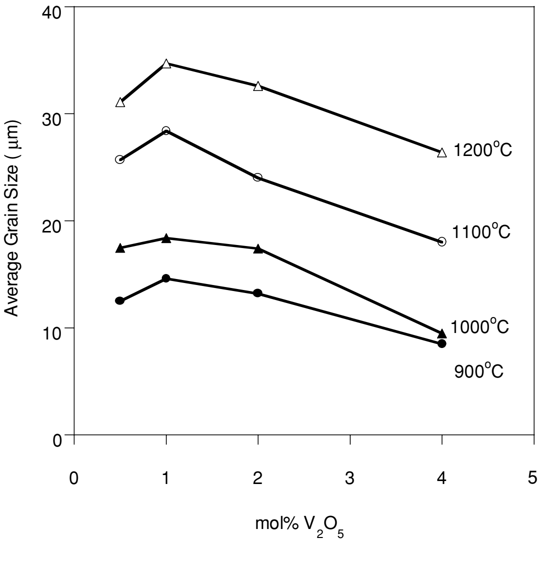

Figure 3 Average ZnO grain size versus V_2O_5 content (in mol%) for samples sintered in air for 4 hrs.

value of 1.44, which is very close to the value of 1.52 obtained in this study. Moreover, our result also agrees well with Tsai and Wu [9], who obtained $1/n$ values ranging from 0.63 to 0.83 (equivalent to n values of 1.20 to 1.59) for 0.5 mol% to 2 mol% V_2O_5. The n values for ZnO-V_2O_5 systems are lower compared to the value of 3 for pure ZnO [21], indicating V_2O_5-doped ZnO has a faster grain growth rate than pure ZnO.

To determine the value of activation energy, Q, for grain growth, Equation 2 can be expressed as

$$\log\left(\frac{G^n}{t}\right) = \log K_o - \frac{0.434Q}{R}\left(\frac{1}{T}\right) \tag{5}$$

so that slopes of the Arrhenius plots of $\log(G^n/t)$ versus $1/T$ yield values of Q for grain growth. To compare the values of Q and K_o for the four compositions, it is necessary to have the same units for these quantities. As n has a direct bearing on the units, particularly those of the preexponential term, K_o, the average n value of the four compositions ($n = 2$) is used to construct the respective Arrhenius plots (Fig. 5). The activation energies Q derived from the slopes of the Arrhenius plots are 90 ± 6 kJ/mol for 0.5 mol% V_2O_5, 87 ± 9 kJ/mol for 1 mol% V_2O_5, 87 ± 6 kJ/mol for 2 mol% V_2O_5, and 115 ± 24 kJ/mol for 4 mol% V_2O_5. The Q values are virtually identical for V_2O_5 content ranging from 0.5–2 mol%, suggesting that the mechanism for ZnO grain growth is identical for all these three V_2O_5-containing compositions. At higher V_2O_5 content, the activiation energy is observed to increase, which indicates a change in the grain growth mechanism. It is also worth noting that the Q values for V_2O_5-containing compositions are consistently lower than the activation energy of pure ZnO, 224 ± 16 kJ/mol [21].

From the plots in Fig. 5, it is also possible to estimate the preexponential term, K_o, in Equation 2. The results of which are summarised in Table I. The preexponential factor contains the concentration of the solid in the liquid, the atomic volume of the solid, the

TABLE I Grain growth parameters

Compositions	n	Q (kJ/mol)	K_o (μm^2/h)
ZnO-0.5 mol% V_2O_5	1.60	90 ± 6	3.9×10^5
ZnO-1 mol% V_2O_5	1.52	87 ± 9	3.7×10^5
ZnO-2 mol% V_2O_5	1.79	87 ± 6	3.0×10^5
ZnO-4 mol% V_2O_5	2.69	115 ± 24	17.3×10^5

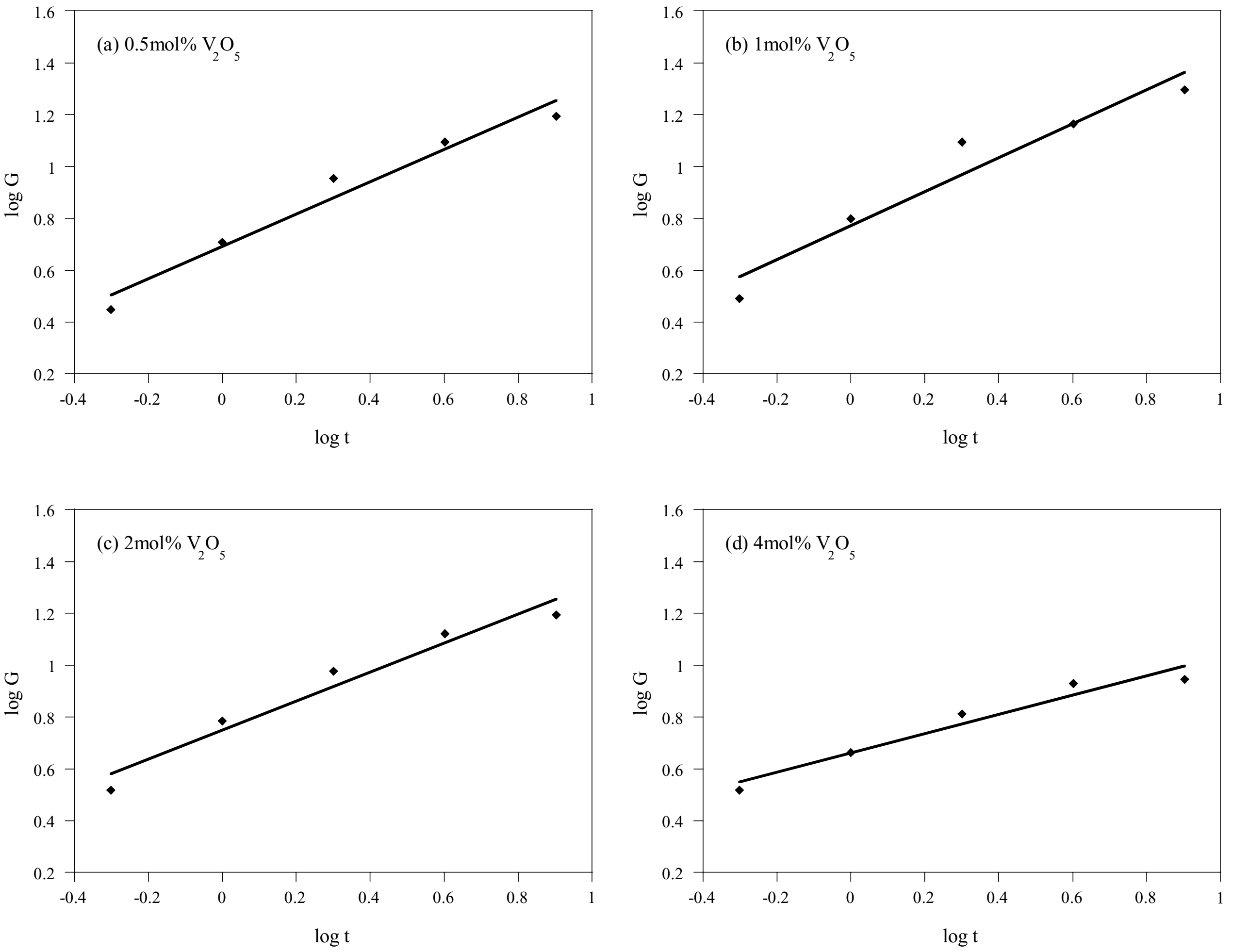

Figure 4 Grain growth of ZnO-V_2O_5 samples sintered at 900°C for various sintering times: (a) 0.5 mol% V_2O_5, (b) 1 mol% V_2O_5, (c) 2 mol% V_2O_5, and (d) 4 mol% V_2O_5.

solid-liquid surface energy, and either the interface reaction rate constant or the diffusivity of the solid through the liquid, depending on the rate controlling process. The K_o values remain rather constant for V_2O_5 content up to 2 mol%, and increases significantly with further V_2O_5 addition to 4 mol%. This further supports the premise that the grain growth mechanism is the same for V_2O_5 compositions up to 2 mol%, and that a change in the rate controlling process is observed for higher V_2O_5 content. Unfortunately, the units of the K_o terms for pure ZnO are not the same as for the V_2O_5-containing compositions, so that term cannot be directly compared.

4. Discussion

It has been shown that the rate-controlling grain growth mechanism in pure ZnO involves solid-state diffusion of the Zn^{2+} cations within the ZnO lattice, and that the apparent activation energy, Q, is about 224 ± 16 kJ/mol [21]. Analyses on ZnO-Bi_2O_3 systems [21, 22] has found that the Q value decreases significantly with small addition of about 0.5 wt% Bi_2O_3, which remains constant up to about 4 wt%, and subsequently increases with further addition of Bi_2O_3. It is claimed that the initial decrease in the Q value is due to the change in the mechanism for ZnO grain growth from solid-state diffusion of Zn^{2+} for pure ZnO to solution-precipitation for the liquid phase sintering in the presence of Bi-rich liquid. As the content of Bi_2O_3 increases, the thickness of liquid layer also increases. For addition of Bi_2O_3 up to 4 wt%, the ZnO grain growth rate is controlled by the solution-precipitation phase boundary reaction. Grain growth with this mechanism is independent of the thickness of the liquid layer, and hence, the grain growth rate is not reduced even though the content of Bi_2O_3 or thickness is increased. However, at higher Bi_2O_3 content >4 wt%, the mechanism changes to diffusion through the intergranular liquid layer. The grain growth rate is now inversely related to the thickness of the liquid layer between grains. As the thickness of liquid layer increases, the increased diffusion distance through liquid layer reduces the rate of ZnO grain growth, as observed in the increase in the Q value.

The Q values of the ZnO-V_2O_5 systems obtained in this current work vary with the V_2O_5 content in a similar manner as the ZnO-Bi_2O_3 system. Initial addition of 0.5 mol% V_2O_5 decreases Q significantly. This value remains rather constant up to 2 mol% V_2O_5, and increases when V_2O_5 content is further increased to 4 mol%. Hence, it is possible to postulate that the ZnO grain growth mechanism varies with V_2O_5 content in a similar way as the ZnO-Bi_2O_3 system. It changes from solid state diffusion of Zn^{2+} for pure ZnO to phase boundary controlled precipitation-solution reaction for V_2O_5 addition of up to 2 mol%. The mechanism

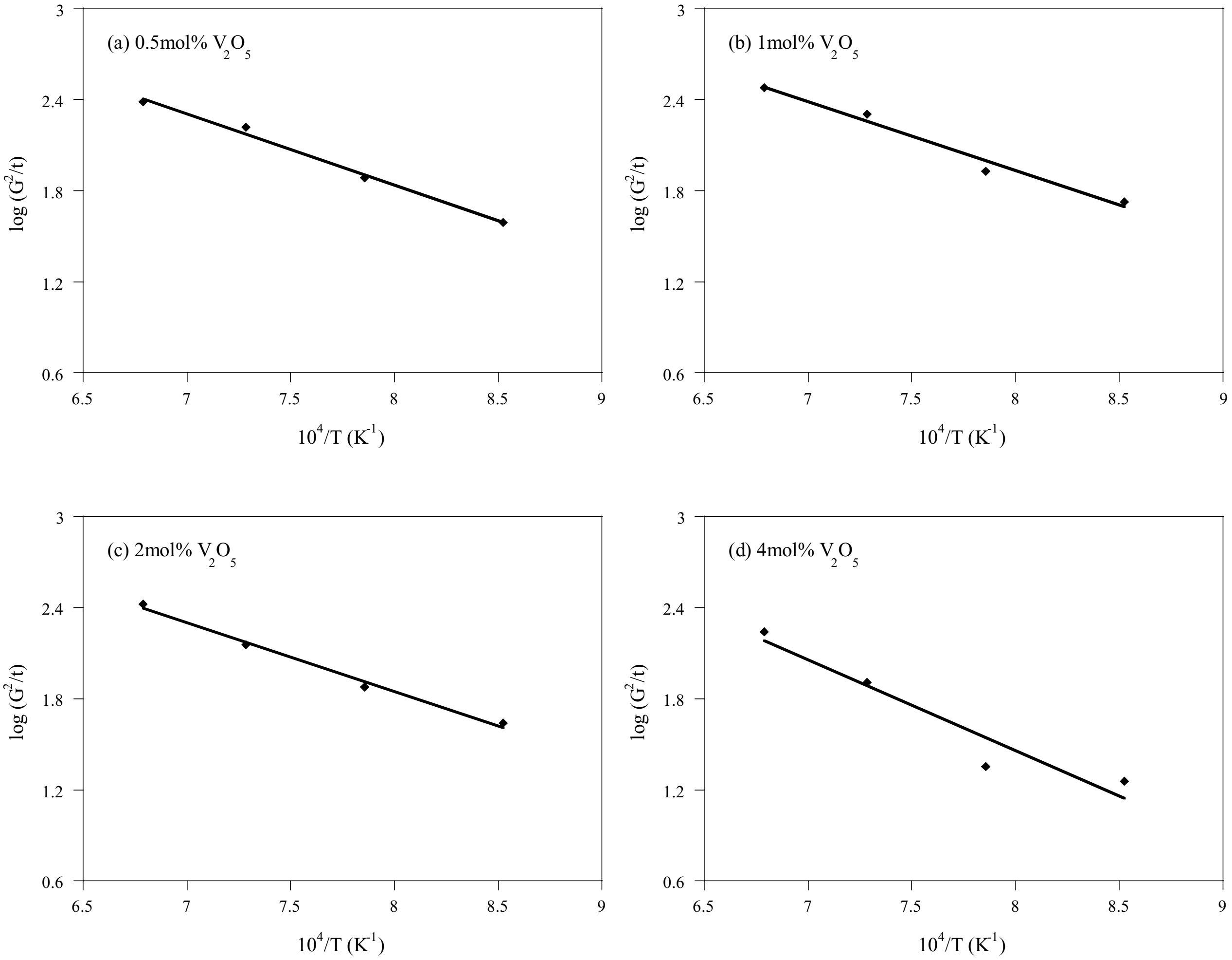

Figure 5 Arrhenius plots for grain growth of ZnO-V_2O_5 ceramics: (a) 0.5 mol% V_2O_5, (b) 1 mol% V_2O_5, (c) 2 mol% V_2O_5, and (d) 4 mol% V_2O_5.

changes to grain boundary controlled when V_2O_5 addition is further increased to 4 mol%. It is also worth noting that Q values for all the ZnO-V_2O_5 systems are lower than that for pure ZnO [21] and ZnO-Bi_2O_3 systems [21, 22]. This indicates that a faster grain growth rate is achieved with V_2O_5 doping.

5. Conclusion

Grain growth behaviour of ZnO during liquid phase sintering of binary ZnO-V_2O_5 ceramics with 0.5 to 4 mol% V_2O_5 has been systematically studied. The ZnO grain size increases as V_2O_5 content is increased up to 2 mol%. Subsequent increase in V_2O_5 content causes a reduction in the grain size. The kinetic grain growth exponent n varies with V_2O_5 content and ranges from 1.52 to 2.69. Q values decrease significantly for V_2O_5-doped ZnO as compared to pure ZnO. For the range of 0.5–2 mol% V_2O_5, $Q$and K_o remains rather constant. Further addition of V_2O_5 increases both Q and K_o values. These results show that mechanism for ZnO grain growth changes with V_2O_5 content. It is postulated that the mechanism changes from solid-state diffusion of Zn^{2+} within the lattice for pure ZnO, to solution-precipitation liquid phase sintering for V_2O_5-doped ZnO. For 0.5–2 mol% of V_2O_5, the reaction is grain boundary controlled solution-precipitation, whereby grain growth is independent of the thickness of liquid layer. It changes to diffusion through intergranular liquid layer as V_2O_5 addition increases to 4 mol%, in which grain growth is liquid thickness dependent.

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